

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>H01M 4/50, 4/62</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/13285</b> <b>(43) International Publication Date:</b> 10 April 1997 (10.04.97)
<b>(21) International Application Number:</b> PCT/IT96/00181 <b>(22) International Filing Date:</b> 30 September 1996 (30.09.96) <b>(30) Priority Data:</b> FI95A000203 3 October 1995 (03.10.95) IT <b>(71) Applicant (for all designated States except US):</b> VOLTA INDUSTRIES S.R.L. [IT/IT]; Via Pisana, 336, I-50010 Badia a Settimo (IT). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> RIZZARDI, Francesco [IT/IT]; Via Donna Rosa, 8, I-20050 Lesmo (IT). <b>(74) Agents:</b> MANNUCCI, Gianfranco et al.; Via della Scala, 4, I-50123 Firenze (IT).		<b>(81) Designated States:</b> BR, CA, JP, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>  <div style="text-align: center; font-size: 2em; margin-top: 50px;">NO</div>
<b>(54) Title:</b> DRY BATTERY HAVING A CATHODE WITH ADDITIVES  <b>(57) Abstract</b>  The battery is of the primary alkaline type and comprises a zinc anode, an anodic gel and a cathode. The cathode comprises a depolarizing mixture based on manganese dioxide containing a mica powder whose grains have a surface at least partially coated with titanium dioxide.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## Dry battery having a cathode with additives

DESCRIPTIONTechnical Field

The present invention relates to a dry battery of the primary alkaline type. More particularly, the invention relates to a battery including a zinc anode, an anodic gel containing an alkaline compound, and a cathode including a depolarizing mixture based on manganese dioxide and graphite.

Background Art

The most recent developments regarding the manufacture of primary alkaline manganese batteries involve the use of titanium dioxide in various allotropic forms as an additive in the depolarizing mixture based on manganese dioxide, which represents the cathode of the battery. Such an additive, which enhances the rate of depolarization on the part of the manganese dioxide in the interior of the cathodic mass, principally has the effect of increasing the output of the battery when the latter is subjected to use with high current consumption.

Objects and Summary of the Invention

The object of the present invention is a further increase - by means of particular additives - of the output of the battery, expressed as the duration of discharge before the discharge tension falls below a preset level. In particular, the present invention provides for the use as additive of a mica powder whose grains have a surface at least partially coated with titanium dioxide, this powder having a particle size distribution of between 1 and 100 micrometres, preferably

- 2 -

between 1 and 15 micrometres.

In a preferred embodiment, the said powder has a content by weight formed from equal parts of titanium dioxide and mica.

Said powder can be present in the depolarizing mixture forming the cathode in a percentage quantity of between 0.1 and 5%, preferably in a percentage quantity of the order of 1%.

The titanium dioxide contained in the said powder can be present in any one of its allotropic forms called anatase, rutile and brookite, also in a mixture of these, and is deposited on the mica grains, for example by dispersing the mica in liquid titanium tetrachloride and then transforming, by means of a known thermochemical process, the titanium tetrachloride into titanium oxide of the desired allotropic form.

With respect to a cathodic mass provided with an additive of only titanium dioxide, the particular structure of the additive proposed according to the present invention - characterized by a high granulometric fineness and, given the particular lamellar configuration of the mica crystals, by a high value of the surface-to-volume ratio of the grains themselves and by surface adhesion of the titanium dioxide particles to the mica particles - provides an increased absorption capacity for liquids and hence electrolyte on the part of the cathodic mass in which the additive is dispersed. For example, with a quantity of 1% of additive in the depolarizing mixture, the absorption capacity of the electrolyte increases by about 8% when passing from an additive composed solely of titanium dioxide to an additive as described above and composed of mica and titanium dioxide in equal parts. The increased quantity of electrolyte contained in the cathode makes higher discharge outputs possible, both for discharges at high consumption and for other types of use.

- 3 -

### Brief Description of the Drawings

The invention will be better understood by following the description and the attached drawing which refers to properties useful in the evaluation of the inventive content of the invention. In the drawing: Figures 1 to 6 show graphs of the discharge of batteries with an additive, respectively, with an additive containing 95% of rutile, the tests for which are marked A in the graphs, and with an additive containing 50% of rutile and 50% of mica mixed with one another in a powder, the tests for which are marked E in the graphs.

### Detailed Description

For comparison of the effectiveness of the additives, tests were carried out under various discharge conditions, both intermittent and continuous, and with loads of varying magnitude (expressed as the electrical resistance in ohm).

For the tests, batteries were prepared comprising: a zinc anode, an anodic gel containing caustic potash, a corrosion inhibitor without added mercury, and a cathode comprising a depolarizing mixture based on manganese dioxide, graphite and the mica powder in which the grains were coated with rutile. To obtain the depolarizing mixture, said components were intimately mixed with one another beforehand in order to ensure a homogeneous distribution in the mixture. For all the batteries, the same constructional criterion was used and the same common components were utilized in order to guarantee the maximum uniformity of the batteries themselves which were produced from a single batch of common materials. The test was carried out with a uniform criterion also with regard to the ageing of the batteries or to the time elapsed from the formation of each battery and the test itself.

- 4 -

In all the tests, the concentration of the additive was kept within 1% relative to the manganese dioxide.

In Figures 1 to 6, the durations in minutes or in hours of effective discharge are indicated on the abscissae. For each test, the result assumed is the time of actual discharge elapsed until the potential of the battery has fallen to the value E.P. (end point) shown on each figure, in accordance with the standard IEC 86/1. For each type of battery, the right-hand border of the hatched area represents in the figures the average of the values obtained with further successive tests.

In all the tests carried out, the values of duration measured show that the batteries of type E (provided with an additive of mica and rutile) give durations which are greater by a value of between 4% and 8% than the durations of the batteries of type A (provided solely with a rutile additive).

- 5 -

## CLAIMS

1. Dry battery of the primary alkaline type, including: a zinc anode; an anodic gel containing an alkaline compound; and a cathode comprising a depolarizing mixture based on manganese dioxide and graphite, characterized in that said mixture contains a mica powder whose grains are coated at least partially with titanium dioxide.
2. Battery according to Claim 1, characterized in that said powder has a particle size distribution of between 1 and 100 micrometres.
3. Battery according to Claim 1 or 2, characterized in that said powder has a particle size distribution of between 1 and 15 micrometres.
4. Battery according to Claims 1 to 3, characterized in that said powder has a content by weight formed from substantially equal parts of titanium dioxide and mica.
5. Battery according to any of the preceding claims, characterized in that said powder is present in said mixture in a percentage quantity of between 0.1 and 5%.
6. Battery according to Claim 4, characterized in that said percentage quantity is of the order of 1%.
7. Battery according to any of the preceding claims, characterized in that the titanium dioxide is present in the allotropic form called anatase.
8. Battery according to any of Claims 1 to 5, characterized in that the titanium dioxide is present in the allotropic form called rutile.
9. Battery according to any of Claims 1 to 5, characterized in that the titanium dioxide is present in the allotropic form called brookite.
10. Battery according to any of Claims 1 to 5, characterized in that the titanium dioxide is present as a mixture of said various allotropic forms.

- 6 -

11. Battery according to any of Claims 1 to 10, characterized in that said alkaline compound is caustic potash or magnesium hydroxide or the like.

12. Battery according to any of Claims 1 to 10, characterized in that it includes corrosion inhibitors and/or a mercury amalgam.



1/2

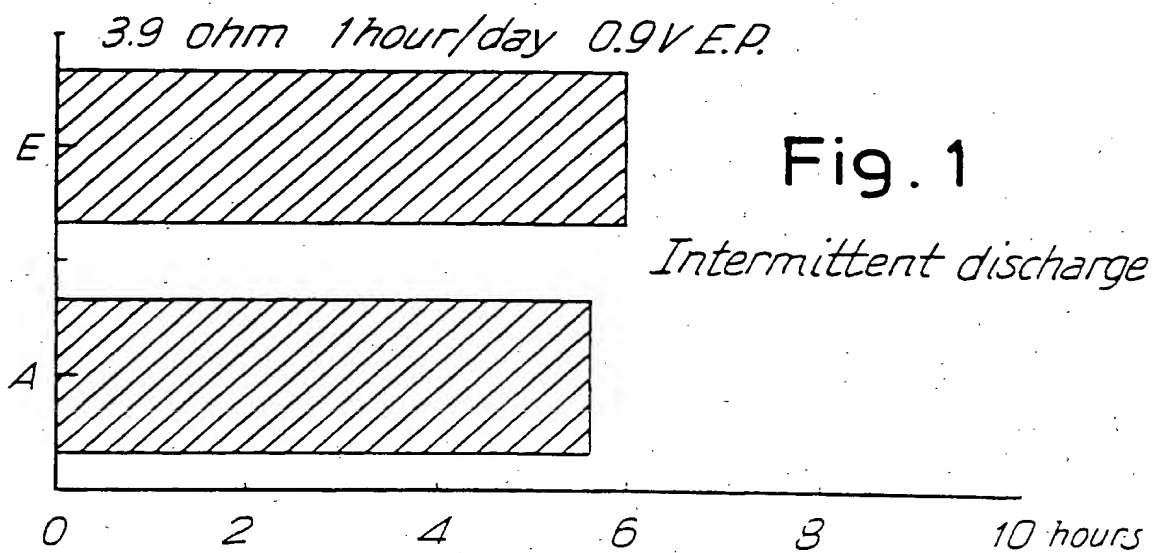


Fig. 2

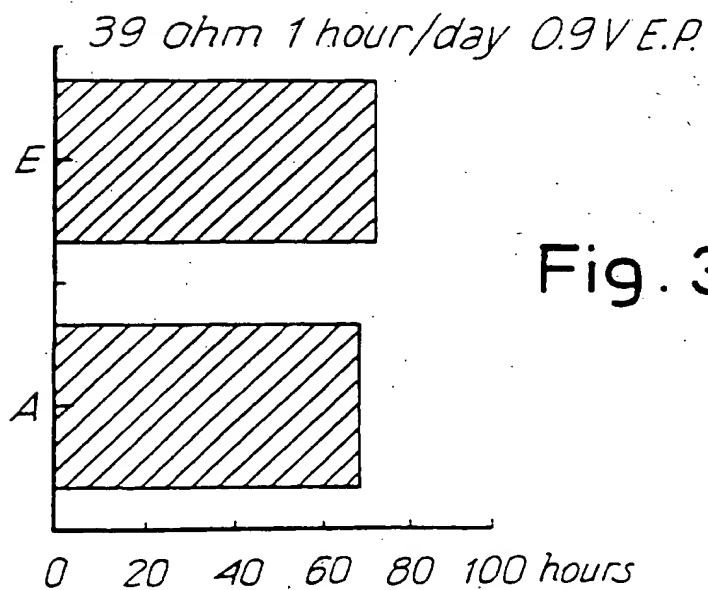
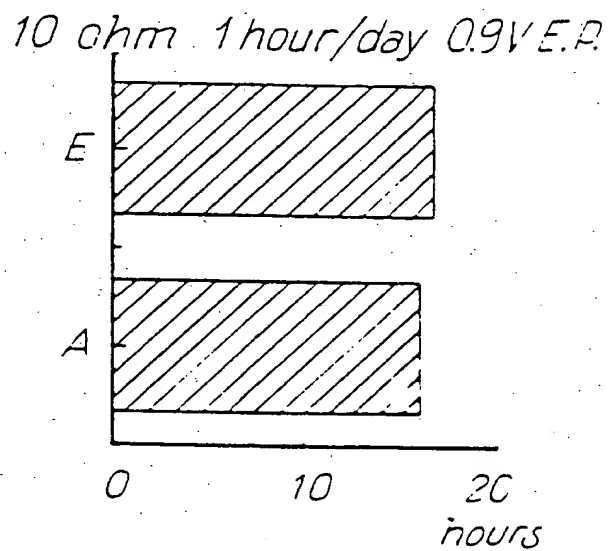


Fig. 3

2/2

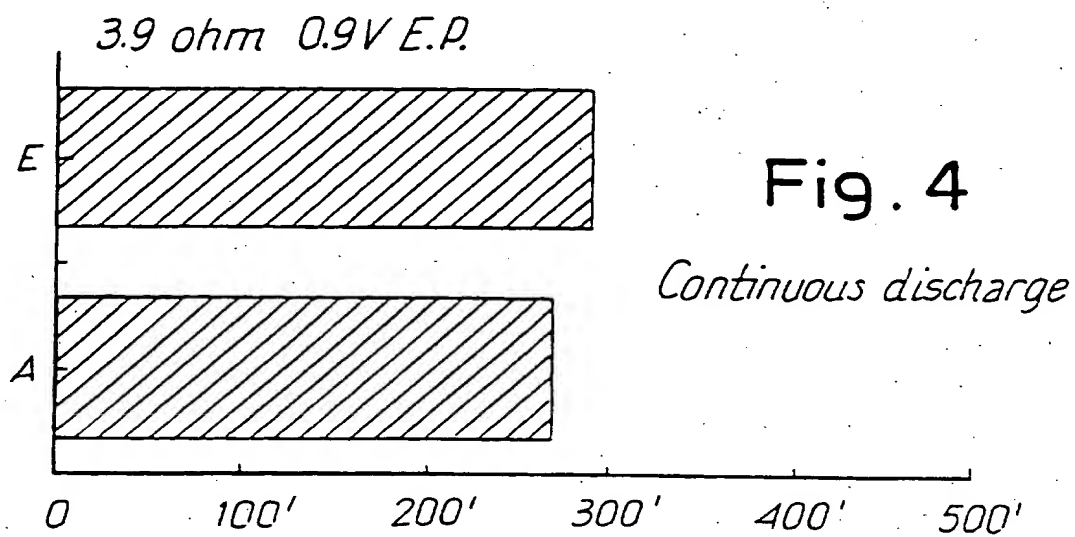
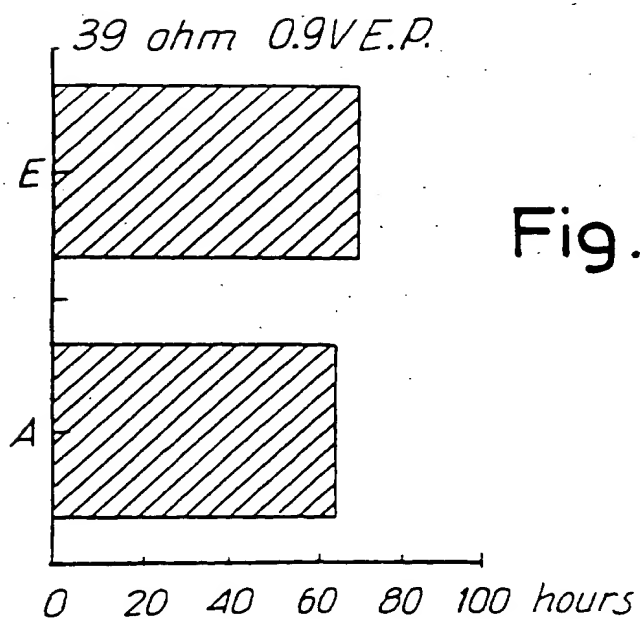
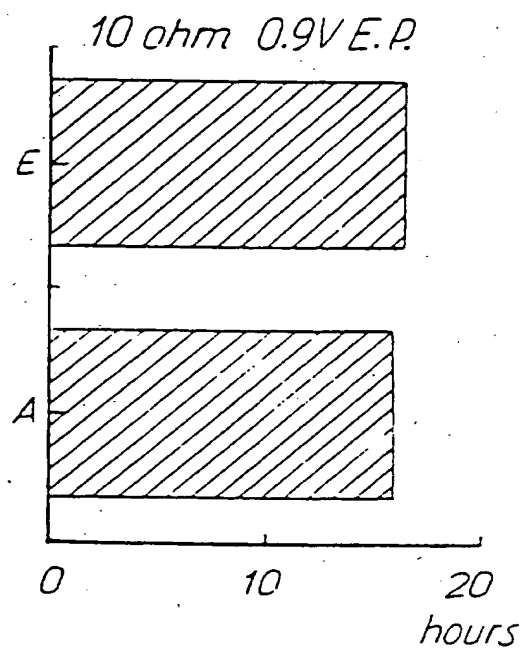


Fig. 5



# INTERNATIONAL SEARCH REPORT

Internal Application No  
PCT/IT 96/00181

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01M4/50 H01M4/62

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 342 712 (MIECZKOWSKA JOLA E ET AL) 30 August 1994 see column 2, line 23 - line 50; claims 1-13 ---	1-12
A	PATENT ABSTRACTS OF JAPAN vol. 009, no. 053 (E-301), 7 March 1985 & JP,A,59 194355 (TOSHIBA DENCHI KK), 5 November 1984, see abstract ---	1-12
A	US,A,5 300 371 (TOMANTSCHGER KLAUS ET AL) 5 April 1994 see column 15, line 29 - line 55; claims 1-49 -----	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*B\* earlier document but published on or after the international filing date
- \*C\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*D\* document referring to an oral disclosure, use, exhibition or other means
- \*E\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

24 January 1997

Date of mailing of the international search report

11. 02. 97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Battistig, M

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal Application No  
PCT/IT 96/00181

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5342712	30-08-94	AU-B- 674090	05-12-96
		AU-A- 6946494	12-12-94
		BR-A- 9406526	02-01-96
		CA-A- 2163101	24-11-94
		CN-A- 1123584	29-05-96
		DE-T- 699347	24-10-96
		EP-A- 0699347	06-03-96
		FI-A- 955507	15-11-95
		JP-T- 8510355	29-10-96
		NZ-A- 267237	25-06-96
		WO-A- 9427332	24-11-94
		ZA-A- 9403176	11-01-95
		-----	
US-A-5300371	05-04-94	US-A- 5108852	28-04-92
		US-A- 5204195	20-04-93
		AU-A- 6152294	08-11-94
		BR-A- 9406476	23-01-96
		CA-A- 2157174	27-10-94
		WO-A- 9424718	27-10-94
		CN-A- 1109641	04-10-95
		EP-A- 0695465	07-02-96
		FI-A- 954995	19-10-95
		JP-T- 8508847	17-09-96
		NZ-A- 262079	20-12-96
		AU-A- 4469293	21-10-93
		AU-B- 640707	02-09-93
		AU-A- 6632590	03-09-91
		WO-A- 9112635	22-08-91
		DE-T- 520990	16-03-95
		EP-A- 0520990	07-01-93
		ES-T- 2055676	01-09-94
		US-A- 5346783	13-09-94
		US-A- 5336571	09-08-94
		-----	